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(54) Method for fabricating a semiconductor structure having a stable crystalline interface with silicon

(57) A method for fabricating a semiconductor structure comprises the steps of providing a silicon substrate (10) having a surface (12); forming on the surface of the silicon substrate an interface (14) characterised by a single atomic layer of silicon, nitrogen, and a metal; and forming one or more layers of a single crystal oxide (26) on the interface. The interface comprises an atomic layer of silicon, nitrogen, and a metal in the form $MSiN_2$, where M is a metal. In a second embodiment, the interface comprises an atomic layer of silicon, a metal, and a mixture of nitrogen and oxygen in the form MSi $[N_{1-x}O_x]_2$, where M is a metal and X is $0 \leq X < 1$.

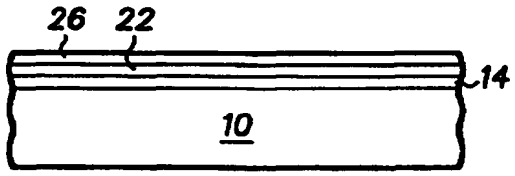

FIG. 10

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Description

Field of the Invention

[0001] The present invention relates in general to a method for fabricating a semiconductor structure including a crystalline alkaline earth metal silicon nitrogen based interface between a silicon substrate and oxides or nitrides, and more particularly to a method for fabricating an interface including an atomic layer of an alkaline earth metal, silicon, and nitrogen.

Background of the Invention

[0002] An ordered and stable silicon (Si) surface is most desirable for subsequent epitaxial growth of single crystal thin films on silicon for numerous device applications, e.g., ferroelectrics or high dielectric constant oxides for non-volatile high density memory and logic devices. It is pivotal to establish an ordered transition layer on the Si surface, especially for subsequent growth of single crystal oxides, e.g., perovskites.

[0003] Some reported growth of these oxides, such as BaO and $BaTiO_3$ on Si(100) was based on a $BaSi_2$ (cubic) template by depositing one fourth monolayer of Ba on Si(100) using reactive epitaxy at temperatures greater than 850°C. See for example: R. McKee et *al., Appl. Phys. Lett.* 59(7), pp 782-784 (12 August 1991); R. McKee et *al., Appl. Phys. Lett.* 63(20), pp. 2818-2820 (15 November 1993); R. McKee et al., *Mat. Res. Soc. Symp.* Proc., Vol. 21, pp. 131-135 (1991); R.A. McKee, F.J. Walker and M.F. Chisholm, "Crystalline Oxides on Silicon: The First Five Monolayers", *Phys. Rev. Lett.* 81 (14), 3014-7 (5 Oct. 1998). U.S. Patent No. 5,225,031, issued July 6, 1993, entitled "Process for Depositing an Oxide Epitaxially onto a Silicon Substrate and Structures Prepared with the Process"; and U.S. Patent No. 5,482,003, issued January 9, 1996, entitled "Process for Depositing Epitaxial Alkaline Earth Oxide onto a Substrate and Structures Prepared with the Process". However, atomic level simulation of this proposed structure indicates that it likely is not stable at elevated temperatures.

[0004] Growth of $SrTiO_3$ on silicon (100) using an SrO buffer layer has been accomplished. T. Tambo et al., *Jpn. J Appl. Phys.*, Vol. 37 (1998), pp. 4454-4459. However, the SrO buffer layer was thick (100 Å), thereby limiting application for transistor films, and crystallinity was not maintained throughout the growth.

[0005] Furthermore, $SrTiO_3$ has been grown on silicon using thick metal oxide buffer layers (60-120 Å) of Sr or Ti. B. K. Moon et al., *Jpn. J. Appl. Phys.*, Vol. 33 (1994), pp. 1472-1477. These thick buffer layers would limit the application for transistors.

[0006] Therefore, a method for fabricating a thin, stable crystalline interface with silicon is needed.

Brief Description of the Drawings

[0007]

FIGs. 1-2 illustrate a cross-sectional view of a clean semiconductor substrate having an interface formed thereon in accordance with the present invention;

FIGs. 3-6 illustrate a cross-sectional view of a semiconductor substrate having an interface formed from a silicon nitride layer in accordance with the present invention; and

FIGs. 7-8 illustrate a cross-sectional view of an alkaline-earth-metal nitride layer formed on the structures illustrated in FIGs. 1-6 in accordance with the present invention.

FIGs. 9-12 illustrate a cross-sectional view of a perovskite formed on the structures of FIGs. 1-8 in accordance with the present invention.

FIG. 13 illustrates a side view of the atomic structure of one embodiment of the layers of FIG. 12 in accordance with the present invention.

FIG. 14 illustrates a top view along view line AA of FIG. 13 of the interface.

FIG. 15 illustrates a top view along view line AA of FIG. 13 including the interface and the adjacent atomic layer of the substrate.

Detailed Description of the Preferred Embodiment

[0008] To form the novel interface between a silicon (Si) substrate and one or more layers of a single crystal oxide or nitride, various approaches may be used. Several examples will be provided for both starting with a Si substrate having a clean surface, and a Si substrate having silicon nitride (Si_3N_4 or the like) on the surface. Si_3N_4 is amorphous rather than single crystalline and it is desirable for purposes of growing additional single crystal material on the substrate that a single crystal nitride be provided as the interface.

[0009] Turning now to the drawings in which like elements are designated with like numbers throughout, FIGs. 1 and 2 illustrate a semiconductor structure including a Si substrate 10 having a clean surface 12. A clean (2x1) surface 12 may be obtained with any conventional cleaning procedure, for example, with thermal desorption of SiO_2 at a temperature greater than or equal to 850°C, or by removal of the hydrogen from a hydrogen terminated Si(1x1) surface at a temperature greater than or equal to 300°C in an ultra high vacuum. Hydrogen termination is a well known process in which hydrogen is loosely bonded to dangling bonds of the silicon atoms at surface 12 to complete the crystalline structure. The interface 14 of a crystalline material may be formed by supplying (as shown by the arrows in FIG. 1) controlled amounts of a metal, Si, and activated nitrogen, either simultaneously or sequentially to the surface 12 at a temperature less than or equal to 900°C in

a growth chamber with N_2 partial pressure less than or equal to $1x10^{-6}$mBar. The metal applied to the surface 12 to form the interface 14 may be any metal, but in the preferred embodiment comprises an alkaline-earth-metal, such as barium (Ba) or strontium (Sr).

[0010] As the application of the Ba, Si, and activated nitrogen form $BaSiN_2$ as the interface 14, the growth is monitored using Reflection High Energy Electron Diffraction (RHEED) techniques which are well documented in the art and which can be used in situ, i.e., while performing the exposing step within the growth chamber. The RHEED techniques are used to detect or sense surface crystalline structures and in the present process change rapidly to strong and sharp streaks by the forming of an atomic layer of the $BaSiN_2$. It will of course be understood that once a specific manufacturing process is provided and followed, it may not be necessary to perform the RHEED techniques on every substrate.

[0011] The novel atomic structure of the interface 14 will be described in subsequent paragraphs.

[0012] It should be understood by those skilled in the art that the temperatures and pressures given for these processes are recommended for the particular embodiment described, but the invention is not limited to a particular temperature or pressure range.

[0013] Alternatively, in forming the interface 14, oxygen may be supplied along with the metal, silicon, and nitrogen to form a mixture. The ratio of nitrogen to oxygen may vary substantially, but preferably would be approximately 80%.

[0014] Referring to FIGs. 3-6, another approach comprises forming a Si substrate 10 having a surface 12, and a layer 16 of silicon nitride thereupon. The layer 16 of silicon nitride can be formed purposely in a controlled fashion known in the art, e.g., by applying (arrows) active nitrogen onto the surface 12. The silicon nitride layer can also be formed on Si substrate using both silicon and active nitrogen in an ultra high vacuum. See for example, R. Droopad, et. al., US Patent No. 5,907,792, issued May 25, 1999, entitled "Method of Forming a Silicon Nitride Layer". The novel interface 14 may be formed at least in one of the two suggested embodiments as follows: By applying an alkaline-earth-metal to the surface 18 of silicon nitride layer 16 at 700-900°C, under an ultra high vacuum. More specifically, the Si substrate 10 and the amorphous silicon nitride layer 16 are heated to a temperature below the sublimation temperature of the silicon nitride layer 16. This can be accomplished in a molecular beam epitaxy chamber or Si substrate 10 can be at least partially heated in a preparation chamber after which it can be transferred to the growth chamber and the heating completed. Once the Si substrate 10 is properly heated and the pressure in the growth chamber has been reduced appropriately, the surface 12 of the Si substrate 10 having silicon nitride layer 16 thereon is exposed to a beam of metal, preferrably an alkaline-earth-metal, as illustrated in FIG. 5. In a preferred embodiment, the beam is Ba or Sr which is generated by resistively heating effusion cells or from e-beam evaporation sources. In a specific example, Si substrate 10 and silicon nitride layer 16 are exposed to a beam of Ba. The Ba joins the silicon nitride and converts the silicon nitride layer 16 into the interface 14 characterised by $BaSiN_2$ in a crystalline form. Alternatively, an alkaline-earth-metal may be provided to the surface 18 at lower temperatures, annealing the result at 700-1000°C, in an ultra high vacuum. In another embodiment, oxygen may be supplied with the nitrogen to form the interface 14, resulting in a crystalline form of $BaSi[N_{1-x}O_x]_2$.

[0015] Once the interface 14 is formed, one or more layers of a single crystal oxide, nitride, or combination thereof, may be formed on the surface of the interface 14. However, an optional layer of an alkaline-earth-metal oxide, such as BaO or SrO, may be placed between the interface 14 and the single crystal oxide. This alkaline-earth-metal oxide provides a low dielectric constant (advantageous for certain uses such as memory cells) and also prevents oxygen from migrating from the single crystal oxide to the Si substrate 10.

[0016] Referring to FIGs. 7 and 8, the formation of alkaline-earth-metal nitride layer 22 may be accomplished by either the simultaneous or alternating supply to the surface 20 of the interface 14 of an alkaline-earth-metal and active nitrogen at less than or equal to 700°C and under N_2 partial pressure less than or equal to $1x10^{-5}$ mBar. This alkaline-earth-metal nitride layer 22 may, for example, comprise a thickness of 50-500 Å.

[0017] Referring to FIGs. 9-12, a single crystal oxide layer 26, such as an alkaline-earth-metal perovskite, may be formed on either the surface 20 of the interface 14 or the surface 24 of the alkaline-earth-metal nitride layer 22 by either the simultaneous or alternating supply of an alkaline-earth-metal oxide, oxygen, and a transition metal, such as titanium, at less than or equal to 700°C under an oxygen partial pressure less than or equal to $1x10^{-5}$ mBar. This single crystal oxide layer 26 may, for example, comprise a thickness of 50-1000 Å and will be substantially lattice matched with the underlying interface 14 or alkaline-earth-metal oxide layer 22. It should be understood that the single crystal oxide layer 26 may comprises one or more layers in other embodiments.

[0018] Referring to FIG. 13, a side view (looking in the $<\bar{1}10>$ direction) of the atomic configuration of the Si substrate 10, interface 14, and alkaline-earth-metal metal oxygen layer 26 is shown. The configuration shown comprises, in relative sizes, for illustrative purposes, from larger to smaller, strontium atoms 30, silicon atoms 32, nitrogen atoms 34, and titanium atoms 36. The Si substrate 10 comprises only silicon atoms 32. The interface 14 comprises metal atoms (which in the preferred embodiment are illustrated as strontium atoms 30), silicon atoms 32, and nitrogen atoms 34. The alkaline-earth-metal nitrogen layer 26 comprises strontium atoms 30, nitrogen (or a combination of nitrogen

and oxygen) atoms 34, and titanium atoms 36.

[0019] Referring to FIG. 14, a top view of the interface along view line AA of FIG. 13, shows the arrangement of the strontium, silicon, and nitrogen atoms 30, 32, 34.

[0020] Referring to FIG. 15, a top view along line AA of FIG. 13, shows the interface 14 and the top atomic layer 11 of the Si substrate 10.

[0021] For this discussion, a monolayer equals 6.8×10^{14} atoms/cm^2 and an atomic layer is one atom thick. It is seen that the interface 14 shown in the FIGs. comprises a single atomic layer, but could be more than one atomic layer, while the Si substrate 10 and the alkaline-earth-metal metal nitrogen layer may be many atomic layers. Note that in FIG. 13, only four atomic layers of the Si substrate 10 and only two atomic layers of the alkaline-earth-metal metal nitride layer 26 are shown. The interface 14 comprises a half monolayer of the alkaline-earth-metal, a half monolayer of silicon, and a monolayer of nitrogen. Each strontium atom 30 is substantially equally spaced from four of the silicon atoms 32 in the Si substrate 10. The silicon atoms 32 in the interface 14 are substantially on a line and equally spaced between the alkaline-earth-metal atoms in the <110> direction. Each silicon atom 32 in the top layer of atoms in the Si substrate 10 is bonded to a nitrogen atom 34 in the interface 14 and each silicon atom 32 in the interface 14 is bonded to two nitrogen atoms 34 in the interface 14. The three-fold bonding coordination of the nitrogen atoms at the interface 14 is satisfied in this interface structure, which greatly lowers the total energy of the interface layer 14, thus enhancing its stability. The interface 14 comprises rows of strontium, silicon, and nitrogen atoms 30, 32, 34 in a 2x1 configuration on a (001) surface of the Si substrate 10, lx in the $<\bar{1}10>$ direction and 2x in the <110> direction. The interface 14 has a 2xl reconstruction.

[0022] A method for fabricating a thin, crystalline interface 14 with silicon 10 has been described herein. The interface 14 may comprise a single atomic layer. Better transistor applications are achieved by the interface 14 being thin, in that the electrical coupling of the overlying oxide layers to the Si substrate 10 is not compromised, and in that the interface 14 is more stable since the atoms will more likely maintain their crystalinity in processing. This alkaline earth metal-Si-nitrogen-based interface also acts as a diffusion barrier to oxygen and other elements.

Claims

1. A method of fabricating a semiconductor structure characterised by the steps of:

   providing a silicon substrate (10) having a surface (12);
   forming on the surface of the silicon substrate an interface (14) characterised by a single atomic layer of silicon, nitrogen or a mixture of nitrogen and oxygen, and a metal; and
   forming one or more layers (26) of a single crystal material on the interface.

2. The method of fabricating a semiconductor structure of claim 1 wherein the interface comprises a single atomic layer of silicon, nitrogen, oxygen, and a metal.

3. The method of fabricating a semiconductor structure of claim I wherein the material comprises one of a nitride, an oxide, and a mixture of a nitride and an oxide.

4. The method of fabricating a semiconductor structure of claim 1 wherein the forming the interface step includes forming a 2xl reconstruction.

5. The method of fabricating a semiconductor structure of claim 1 wherein the forming the interface step includes forming a surface with a 2xl reconstruction.

6. The method of fabricating a semiconductor structure of claim 1 wherein the forming an interface step includes forming the interface in an ultra-high-vacuum system.

7. The method of fabricating a semiconductor structure of claim 1 wherein the forming an interface step includes forming the interface in a chemical vapor deposition system.

8. The method of fabricating a semiconductor structure of claim 1 wherein the forming an interface step includes forming the interface in a physical vapor deposition system.

9. The method of fabricating a semiconductor structure of claim 1 wherein the forming an interface step comprises forming a single atomic layer comprises silicon, nitrogen, oxygen, and an alkaline-earth-metal.

10. The method of fabricating a semiconductor structure of claim 1 wherein forming an interface step comprises the steps of:

    forming a half of a monolayer of an alkaline-earth-metal;
    forming a half of a monolayer of silicon; and
    forming a monolayer of nitrogen.

11. The method of fabricating a semiconductor structure of claim 1 wherein the forming an interface step comprises the step of forming one or more monolayers of a mixture of oxygen and nitrogen.

12. The method of fabricating a semiconductor structure of claim 1 wherein the single crystal material comprises oxides, nitrides, or a mixture of oxides and nitrides.

13. The method of fabricating a semiconductor structure of claim 1 wherein the single crystal material comprises one or more layers of oxides, nitrides, or a mixture of oxides and nitrides.

14. The method of fabricating a semiconductor structure of claim 1 wherein the single crystal material comprises alkaline-earth-metal oxides.

15. The method of fabricating a semiconductor structure of claim 1 wherein the single crystal material comprises perovskites.

16. The method of fabricating a semiconductor structure of claim 1 wherein the forming an interface step comprises forming a single atomic layer comprises silicon, nitrogen, and an alkaline-earth-metal.

17. The method of fabricating a semiconductor structure of claim 16 wherein the alkaline-earth-metal is selected from the group of barium and strontium.

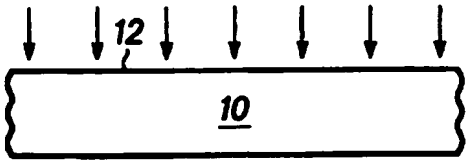

FIG. 1

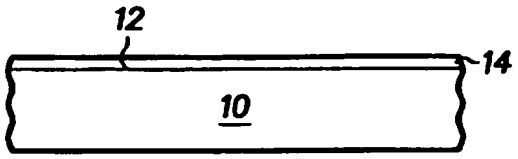

FIG. 2

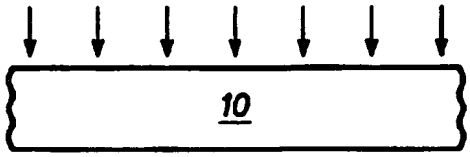

FIG. 3

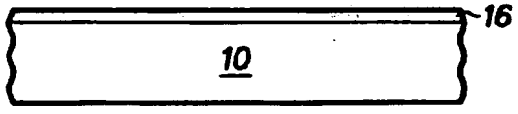

FIG. 4

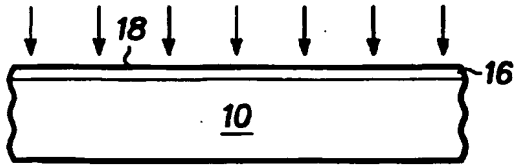

FIG. 5

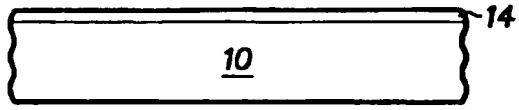

FIG. 6

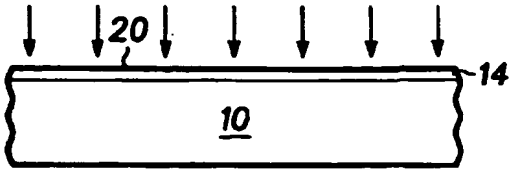

FIG. 7

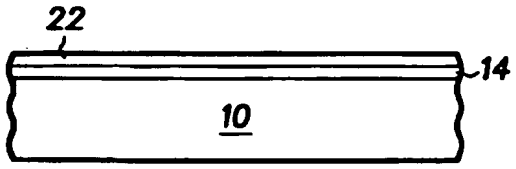

FIG. 8

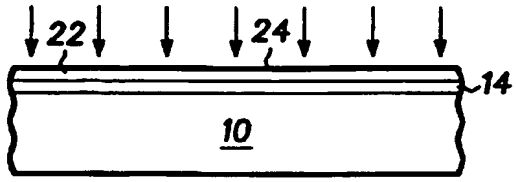

FIG. 9

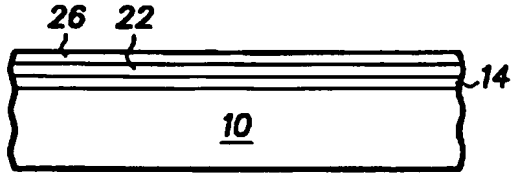

FIG. 10

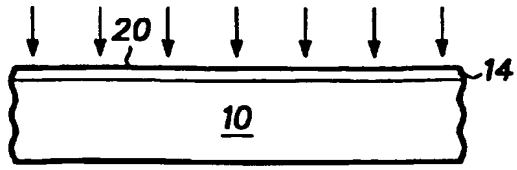

FIG. 11

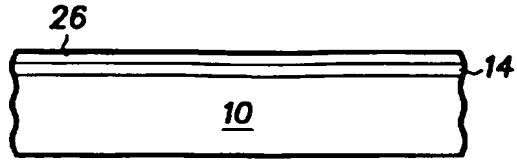

FIG. 12

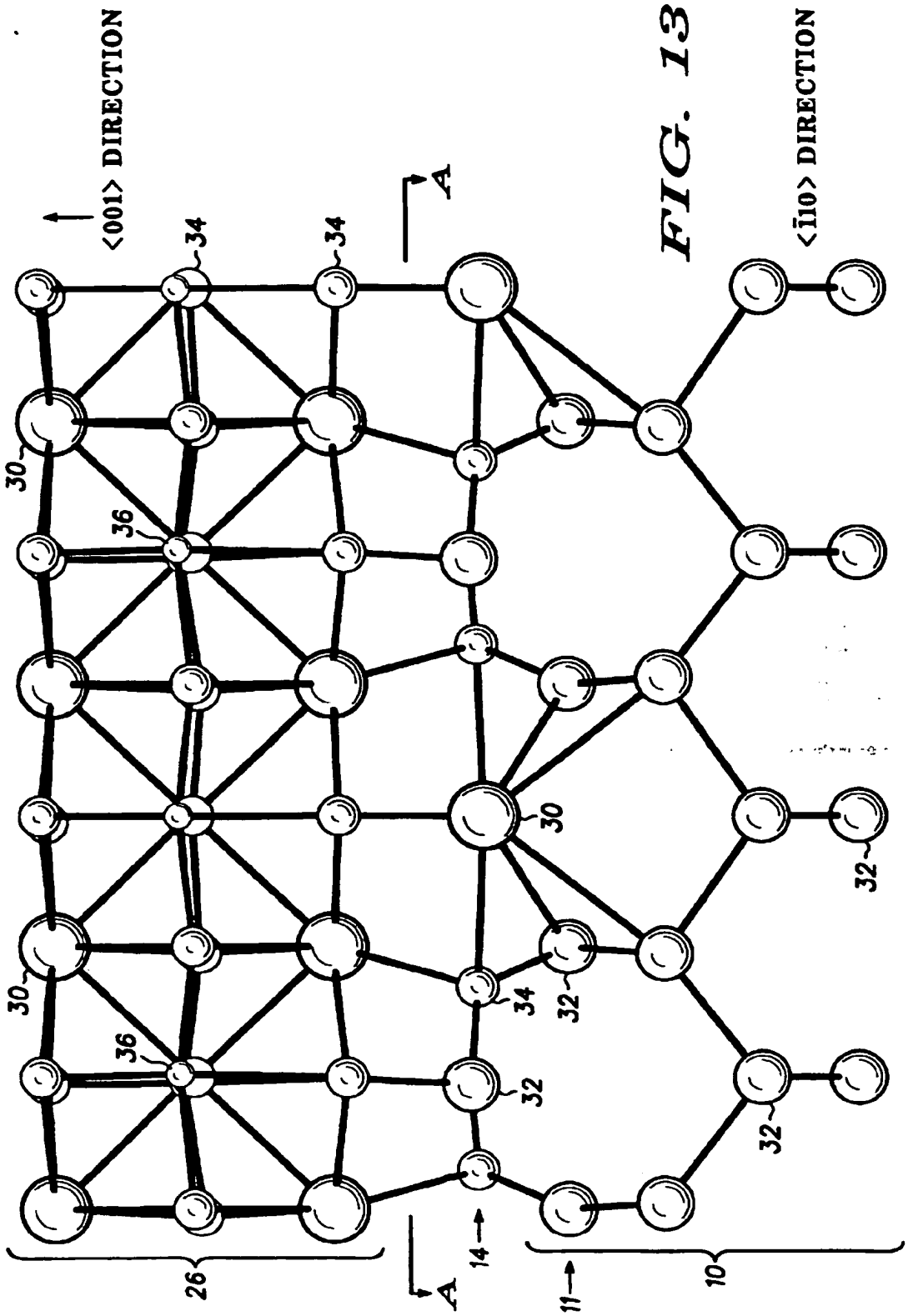

FIG. 13

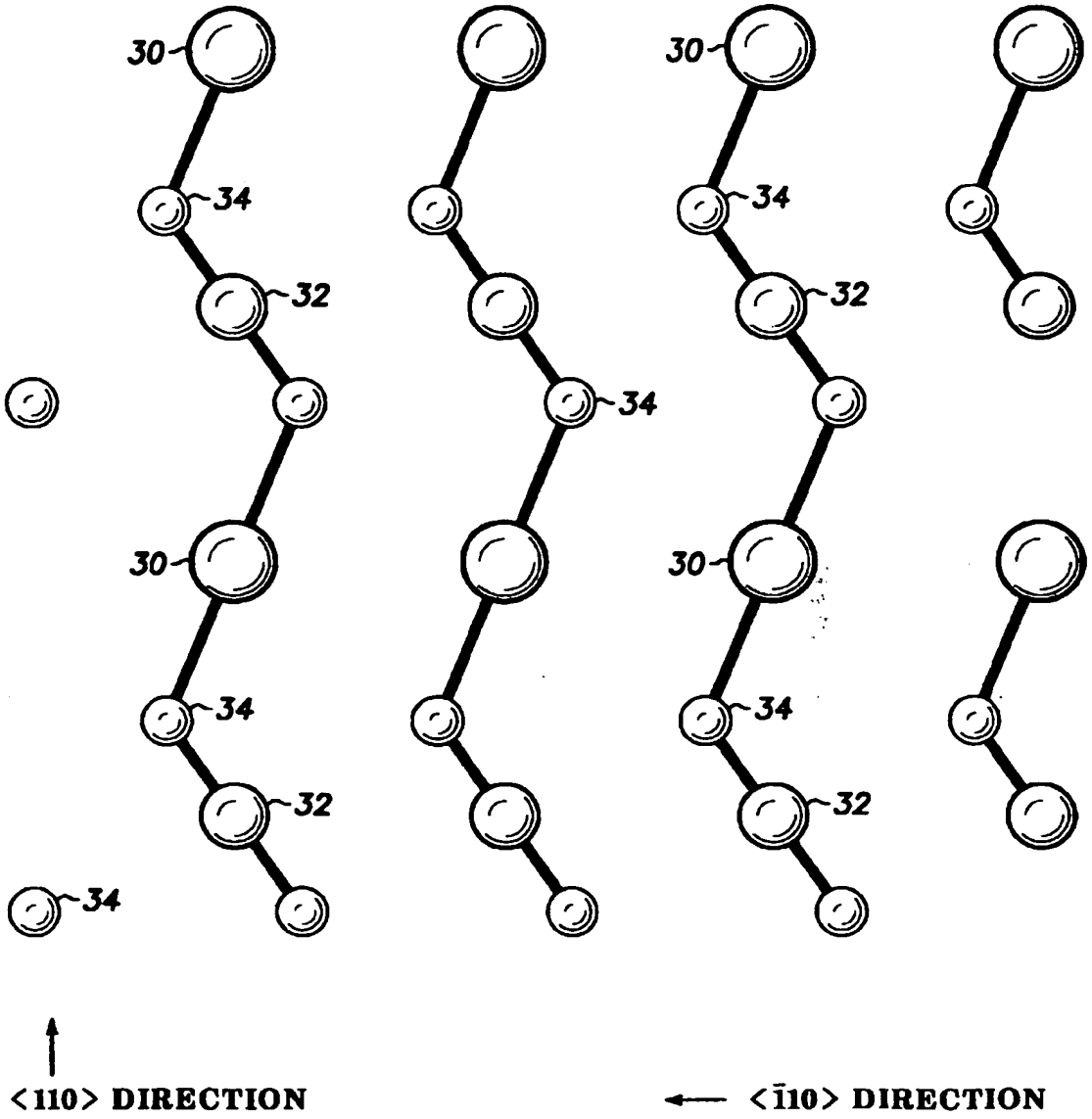
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FIG. 14

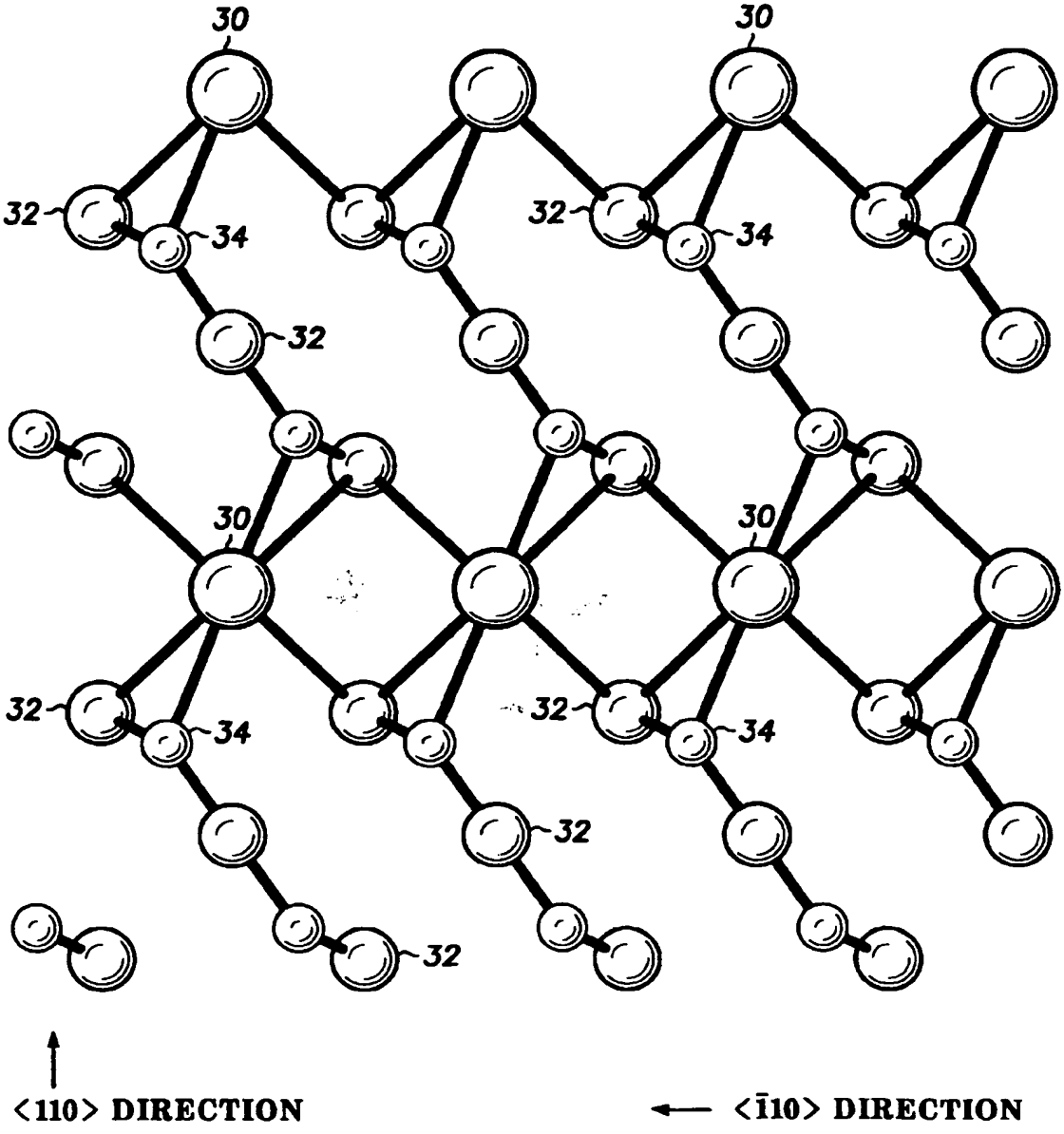
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FIG. 15

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EUROPEAN SEARCH REPORT

Application Number
EP 00 12 7055

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A	MYUNG-BOK LEE ET AL: "HETEROEPITAXIAL GROWTH OF BATIO3 FILMS ON SI BY PULSED LASER DEPOSITION" APPLIED PHYSICS LETTERS,US,AMERICAN INSTITUTE OF PHYSICS. NEW YORK, vol. 66, no. 11, 13 March 1995 (1995-03-13), pages 1331-1333, XP000503592 ISSN: 0003-6951 * page 1333, right-hand column *	1	
A,D	MCKEE R A ET AL: "MOLECULAR BEAM EPITAXY GROWTH OF EPITAXIAL BARIUM SILICIDE, BARIUM OXIDE, AND BARIUM TITANATE ON SILICON" APPLIED PHYSICS LETTERS,US,AMERICAN INSTITUTE OF PHYSICS. NEW YORK, vol. 59, no. 7, 12 August 1991 (1991-08-12), pages 782-784, XP000233755 ISSN: 0003-6951 * the whole document *	1	TECHNICAL FIELDS SEARCHED (Int.Cl.7) C30B H01L
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	23 March 2001	Cook, S

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Application Number
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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
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A	PATENT ABSTRACTS OF JAPAN vol. 1996, no. 04, 30 April 1996 (1996-04-30) & JP 07 330487 A (FUJI XEROX CO LTD), 19 December 1995 (1995-12-19) * abstract *		

TECHNICAL FIELDS SEARCHED (Int.Cl.7)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
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